



The influence of sulfur dioxide and water on the performance of a marine SCR catalyst

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ABSTRACT

This study investigates how sulfur affects the NO_x reduction activity over a commercial vanadium based urea-SCR catalyst for marine applications, especially at low temperatures, and in combination with H₂O. The addition of SO₂ in the absence of H₂O promotes the NO_x reduction at 350 °C, while the addition of H₂O, in the absence of SO₂, gives rise to a decrease in the NO_x reduction and also an inhibition of the N₂O formation. The same trends are observed at transient temperatures, but no promotional effect by SO₂ is seen at temperatures below 230 °C. Further, long term effects of SO₂ and H₂O were investigated and the NO_x reduction remains stable, also after long term exposure of SO₂. The ammonia desorption is investigated using temperature programmed desorption (TPD) experiments, both in the presence and in the absence of SO₂. In general in the presence of both H₂O and SO₂ the catalyst does not show any sign of deactivation at temperatures above 300 °C and fairly low space velocities (below 12,200 h⁻¹). However, at lower temperatures (250 °C) and/or higher space velocities the catalytic performance for NO_x reduction decreases with time.

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1. Introduction

The growing awareness of environmental pollution, such as nitrogen oxides (NO_x), causing eutrophication and acidification at land and sea [1], has contributed to the development of more stringent international NO_x legislations, of which IMO's (International Maritime Organization) Revised MARPOL (Marine Pollution) Annex VI [2] will significantly influence the shipping community. The most stringent NO_x legislation, Tier III, which will enter into force the 1st of January 2016, has given rise to an increased demand on NO_x abatement technology for marine applications.

The upcoming Tier III will likely lead to the use of several NO_x abatement technologies, of which some are not able to reach the Tier III level by themselves. Several different technologies are available on the market [3], such as basic and advanced internal engine modifications (IEM), exhaust gas recirculation (EGR), direct water injection (DWI) and humid air motor (HAM). However, the most effective NO_x abatement technology on the market is selective catalytic reduction (SCR) using a base-metal catalysts and urea as reducing agent. Already in 1957 it was discovered that ammonia could be used to catalytically remove NO_x from lean exhaust

gases [4]. The technique was first used to clean exhaust gases from stationary sources such as power plants and chemical plants. During the last 15–20 years ammonia-SCR has been extensively investigated for reduction of NO_x from heavy-duty vehicles [4–7]. Depending on application there are different possibilities for the ammonia source, e.g. liquefied ammonia, ammonium carbamate, urea dissolved in water and solid urea [7]. In Europe, an infrastructure for the reducing agent (for heavy-duty vehicles) is developed and then the choice is urea dissolved in water [7]. Many catalyst formulations have been investigated for ammonia-SCR and base metal oxides are among the most common commercial ones. The predominant component in such catalysts is vanadium oxide supported on titanium oxide [7], which is the choice for marine applications. Other materials like zeolites have been investigated in this context and for instance Cu-ZSM-5 is found to be active in a broader temperature range compared to vanadium-based catalysts, however, the long-term stability and sulfur resistance may be a problem [7].

The main challenges for SCR in marine applications lies in deactivation and low-temperature activation. The latter is also a problem for cars, trucks and non-road applications and may imply that the catalyst remain inactive during e.g. start-up and maneuvering. The deactivation problem, although SCR catalysts are relative resistant, can be particularly problematic for marine applications where the fuels are residual products that are not well specified, and the urea solution may contain impurities.

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Table 1
Dimensions of sample A and sample B.

Sample	Cross section area [mm ²]	Length [mm]	cpsi	Number of cells
A	330.5	59.5	25	12
B	2601	34.5	25	100

Further, the low-temperature activity may be further hampered by the presence of impurities (sulfur, salts etc.) in the exhaust. According to Kuiken [8], a typical exhaust gas composition (in vol%) for a two-stroke crosshead engine is 13% O₂, 75.8% N₂, 5.2% CO₂, 5.35% H₂O, 1500 ppm NO_x, 600 ppm SO_x, 60 ppm CO, 180 ppm HC and in addition 120 mg/Nm³ of particulate matter. However, the SO₂ concentration varies with the sulfur content in the fuel used which is in the range 0.1–3 wt.% S, giving rise to an approximate range of 20–650 ppm SO₂ in the exhaust. Furthermore, SCR for marine applications are usually not applied in combination with PM-filters and/or pre-oxidation catalyst. However, sometimes an oxidation catalyst is placed downstream of the SCR in order to reduce the NH₃-slip and also the CO emissions.

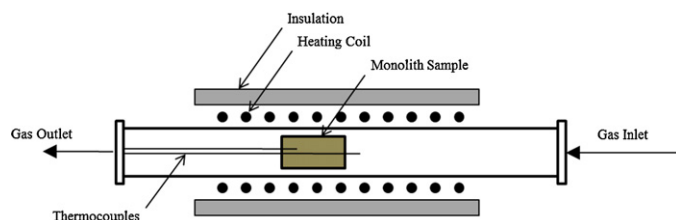
The major part of the scientific research on urea/ammonia-SCR has been devoted to stationary sources and vehicles. The scientific literature on marine applications is sparse, and even though the technique for land-based applications is similar to the marine applications, the boundary conditions are widely differing. However, the impact of sulfur in the exhaust gas on the catalytic activity has been studied for vanadium-based catalysts for stationary sources; see e.g. [9–13], which is also relevant for marine applications. It was, for instance, found that the NO_x reduction is unaffected and high when either water or SO₂ is present in the feed over a pre-sulfated vanadium-based monolith [10,11]. In the presence of both sulfur dioxide and water, on the other hand, the activity for the NH₃-SCR reaction was found to decrease [9,14]. In urea-SCR applications, formation of solid material that can clog pores of the catalyst is a potential problem. For instance, the formation of ammonium sulfate salts has been studied by Huang et al. [12] over vanadium-based catalysts and it was found that these compounds are formed in the presence of both SO₂ and water at low temperatures (around 250 °C). Furthermore, a few studies have been performed for other poisonous compounds than sulfur. Nicosia et al. [14] studied the effect of urea impurities, like potassium, calcium and phosphate, on the NH₃-SCR reaction and the deactivation caused by potassium chloride was studied by Zhang et al. [15].

The aim of this study is to investigate how sulfur affects the NO_x reduction activity over a commercial urea-SCR catalyst for marine applications, especially at low temperatures, and in combination with H₂O.

2. Experimental methods

2.1. Catalyst samples

The SCR catalyst samples in the present study were cut from a commercial titanium oxide (TiO₂)-supported vanadium oxide/tungsten oxide (V₂O₅/WO₃)-based, washcoated urea-SCR

**Fig. 1.** Laboratory-scale flow reactor system.**Table 2**
(a–n) Detailed description of the presented experiments.

Type of experiment	Sample	SV (h ⁻¹)	Temperature (°C)	SO ₂ (ppm)	H ₂ O (%)
Steady-state activity					
Steady-state activity (a)	A (pre-oxidation for 20 min)	6100, 12,200, 18,300	250, 300, 350	0	0
Steady-state activity (b)	B	5700	250, 300, 350	0	0
Steady-state activity including SO ₂ and H ₂ O					
Cyclic variation of SO ₂ (c)	A, B	6100, 5700 (respectively)	350	5 × (1 h 0; 0.5 h 100)	0
Transient SO ₂ (d)	A	12,200	350	0.5 h each: 0; 100; 0; 200; ... 0;	0
	A	12,200	350	1000; 0; 1100	0.5 each 0; 2; 4; 6 (6% CO ₂)
Influence of CO ₂ and H ₂ O (e)	A	12,200	350	0	0
Catalytic activity with transient temperature					
Transient temperature with SO ₂ (f)	A	12,200	400 → 100 and 100 → 400 (10 °C/min)	0; 100; 500; 1000	0
Transient temperature with H ₂ O (g)	A	12,200	400 → 100 and 100 → 400 (10 °C/min)	0	4
Catalytic recovery after SO ₂ exposure and long term effects of SO ₂ and H ₂ O					
Recovering after SO ₂ exposure (h)	A	12,200	350	1 h 500; 6 h 0	0
Long term effect of SO ₂ (i)	A	6100	350	15 h 500	0
Long term effect of H ₂ O (j)	A	6100	350	0	15 h 4
Catalytic activity with transient temperature and space velocity and simultaneous introduction of SO ₂ and H ₂ O					
Long term effect of SO ₂ and H ₂ O; 3 different temperatures (k)	A (pre-oxidation at 350 °C)	6100	250, 300, 350 (5 h each temp)	500	4
Long term effect of SO ₂ and H ₂ O; 2 different SV (l)	A (pre-oxidation at 350 °C)	12,200, 18,300 (5 h each SV)	300	500	4
Catalytic activity with transient temperature and SO ₂ content (m)	A (pre-oxidation at 350 °C)	6100	250, 300, 350 (2 h each temp)	250; 750	4
Temperature programmed desorption (TPD)					
TPD with NH ₃ and SO ₂ (n)	A	12,200	44 → 550 °C, (10 °C/min)	0; 500	0

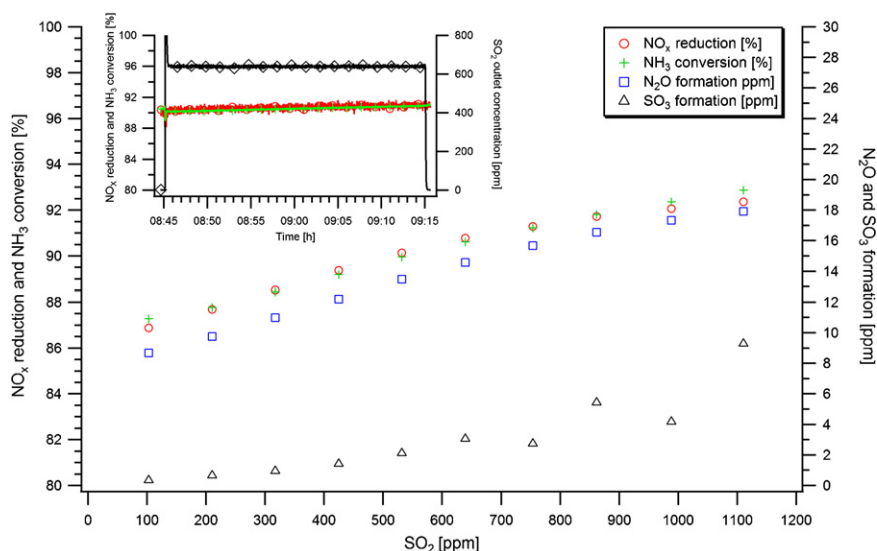


Fig. 2. Influence of the SO_2 concentration on the NO_x reduction performance over sample A. Feed gas composition: 500 ppm NO , 500 ppm NH_3 , 8% O_2 and 100–1100 ppm SO_2 (350°C and $12,200\text{ h}^{-1}$).

catalyst for marine applications provided by D.E.C. Marine AB. In order to enable experiments over a range of space velocities (SV) the catalyst was machined into two samples of different sizes (Table 1) (samples A and B).

2.2. Flow reactor experiments

The flow reactor consisted of a horizontal quartz tube heated by a heating coil (Fig. 1), with an outer diameter corresponding to either 25 or 78 mm, for samples A and B, respectively. The inlet and sample temperatures were measured by thermocouples (type K), approximately 15 mm before the sample and inside the monolith sample (just before the rear end), respectively. All stated temperatures in this study are inlet values. The inlet gas composition was controlled by mass flow controllers (Bronkhorst High-Tech) and the outlet gas composition was analyzed by an MKS MultiGas 2030 HS FTIR instrument. For the experiments with both water and SO_2 in the feed gas, a Horiba PG-250 instrument was used to analyze the outlet gas composition. The PG-250 uses non-dispersive IR detection for CO , SO_2 , and CO_2 ; chemiluminescence (cross-flow modulation) for NO_x ; and a galvanic cell for O_2 measurements.

Prior to all flow reactor experiments the samples were pre-oxidized in 8% O_2 (Ar bal.) at 550°C (or 350°C when the Horiba instrument was used) for 1 h. The inlet gas composition consisted of 500 ppm NO , 500 ppm NH_3 , 8% O_2 , with varying concentrations of SO_2 (0–1000 ppm) and H_2O (0–6%), balanced with Ar. The temperature and SV were also varied. The different experiments are listed

in Table 2. Further, temperature programmed desorption (TPD) experiments were performed over sample A in order to evaluate the ammonia desorption in the absence and presence of SO_2 . After pre-treatment, NH_3 (500 ppm) was adsorbed ($\text{SV } 12,200\text{ h}^{-1}$ and 44°C) for 1.5 h. The sample was then purged with Ar for 1.25 h to remove the physically adsorbed NH_3 . A temperature ramp ($44 \rightarrow 550^\circ\text{C}$, $10^\circ\text{C}/\text{min}$) was then performed in either Ar or in SO_2 (500 ppm) and Ar.

3. Results

3.1. Steady-state activity for ammonia-SCR with/without SO_2 , H_2O and CO_2

Steady state measurements (Table 2a and b) were conducted for samples A and B in order to investigate the influence of the space velocity and temperature on the catalytic activity for lean NO_x reduction with ammonia. The results are summarized in Table 3. It can be seen that the activity decrease with lower temperature and higher space velocity, and in addition it can be noted that sample A ($\text{SV } 6100\text{ h}^{-1}$) and B ($\text{SV } 5700\text{ h}^{-1}$) show very similar NO_x reduction performance. The slight increase over sample B may be attributed to the somewhat lower space velocity.

In order to investigate the potential effect of SO_2 on the catalytic activity, steady state measurements were performed for samples A and B with cyclic variation of SO_2 (Table 2c). The results show stable

Table 3

Steady state NO_x reduction over sample A and B. Feed gas composition: 500 ppm NO , 500 ppm NH_3 and 8% O_2 .

Sample	SV [h^{-1}]	Reaction temperature [$^\circ\text{C}$]	NO_x reduction [%]	NH_3 conversion [%]	N_2O formation [ppm]
Sample A	6100	350	97.1	98.3	5.5
	6100	300	97.3	96.8	3.4
	6100	250	93.4	91.3	3.3
Sample A	12,200	350	88.6	90.3	5.9
	12,200	300	87.0	86.9	3.3
	12,200	250	76.3	75.8	3.1
Sample A	18,300	350	79.2	81.5	6.4
	18,300	300	76.3	77.0	3.3
	18,300	250	63.5	64.5	2.9
Sample B	5700	350	98.7	95.2	6.1
	5700	300	98.3	94.1	3.3
	5700	250	93.8	89.2	2.6

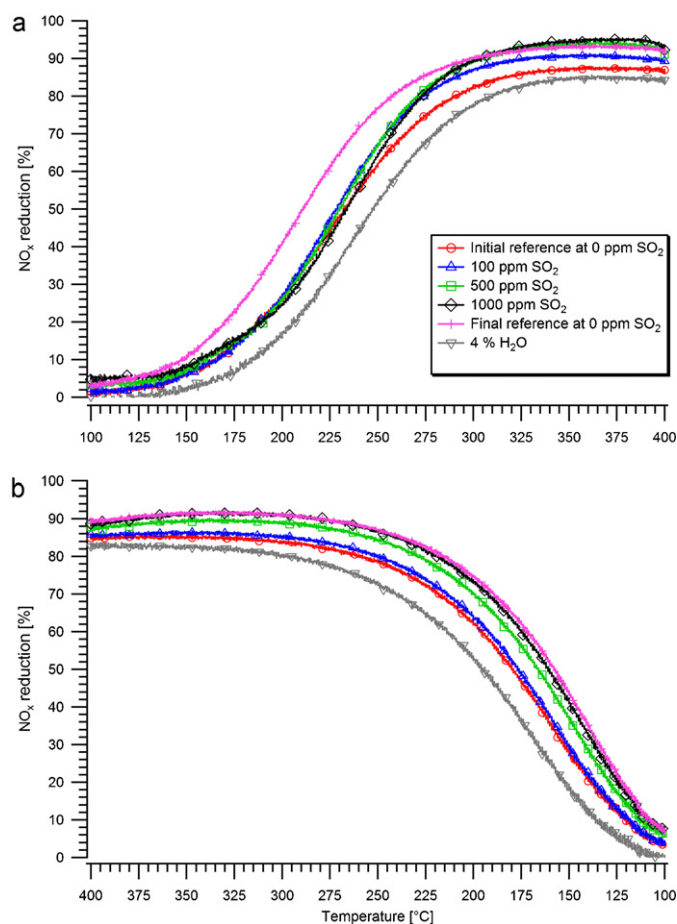


Fig. 3. Catalytic activity for lean NO_x reduction as a function of temperature (a) 100–400 °C and (b) 400–100 °C).

NO_x reduction activity in the range of 98–99%, comparable to the catalytic performance without SO_2 .

Furthermore, the catalytic activity for NO_x reduction was studied for increasing SO_2 concentrations (100–1100 ppm) over sample A (Table 2d). The results are shown in Fig. 2, where it can be seen that the SCR activity increases from about 87% to 92% as the SO_2 concentration increases from 100 ppm to 1100 ppm. Also the SO_3 concentration is shown and can be seen to be about 1% of the inlet SO_2 concentration.

The effects of H_2O and CO_2 on the catalytic activity were also investigated for sample A (Table 2e). The results obtained with H_2O added to the feed gas are summarized in Table 4. Considering the influence of H_2O and CO_2 on the NO_x reduction performance it can be noted that the effect of H_2O on the catalytic activity is two folded; both a decrease of the NO_x reduction rate and an inhibition of the N_2O formation. Further, the effect of H_2O seems to be fairly independent of the H_2O concentration.

Finally, the introduction of CO_2 was investigated and did not give rise to any significant changes in the catalytic activity.

3.2. Influence of transient temperature on the catalytic activity for NO_x reduction

The influence on the lean NO_x reduction activity upon transient temperature changes with SO_2 or H_2O present in the gas feed (Table 2f and g) are presented in Fig. 3. The experiment started with the cooling process, ramping from 400 °C to 100 °C, followed by the opposite heating process. This was done for several sulfur concentrations (0, 100, 500, 1000 ppm), starting and finishing with 0 ppm

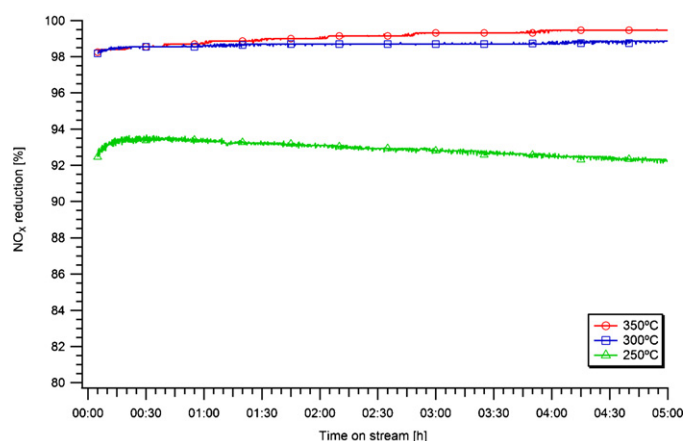


Fig. 4. NO_x reduction at 350 (○), 300 (□) and 250 °C (△). Feed gas composition: 500 ppm NO, 500 ppm NH_3 , 8% O_2 , 500 ppm SO_2 and 4% H_2O (SV 6100 h^{-1}).

sulfur. The sample was then conditioned (oxidized) in 8% O_2 (Ar bal.) at 550 °C for 1 h, to ensure removal of sulfur compounds from the sample, followed by the equivalent cooling/heating process in the presence of 4% H_2O . It can be seen that during the cooling process the catalytic activity increases with increasing concentration of SO_2 . During heating, on the other hand, the activity increase, with increasing SO_2 concentration, starts at around 240 °C and becomes higher above 275 °C. In the presence of H_2O the catalytic activity shows a constant decrease in the whole temperature range.

3.3. Long term effects of SO_2 and H_2O on the catalytic NO_x reduction

The prolonged effect of SO_2 exposure was investigated over sample A (Table 2h). During an hour, in the presence of SO_2 , the NO_x reduction increased slightly (from 85% to 88%). This increase in activity was then sustained during the following 6 h in the absence of SO_2 .

When continuously adding SO_2 or H_2O , separately, to the gas feed (Table 2i and j) over sample A, the lean NO_x reduction performance is stable, corresponding to 99 and 97% for SO_2 and H_2O , respectively.

The long term influence on the catalytic activity for NO_x reduction was also investigated with SO_2 and H_2O added to the gas feed simultaneously (Table 2k–m). The influences of temperature, space velocity and SO_2 are presented in Figs. 4–6, respectively. It was found that the catalytic activity remains high (98%) and

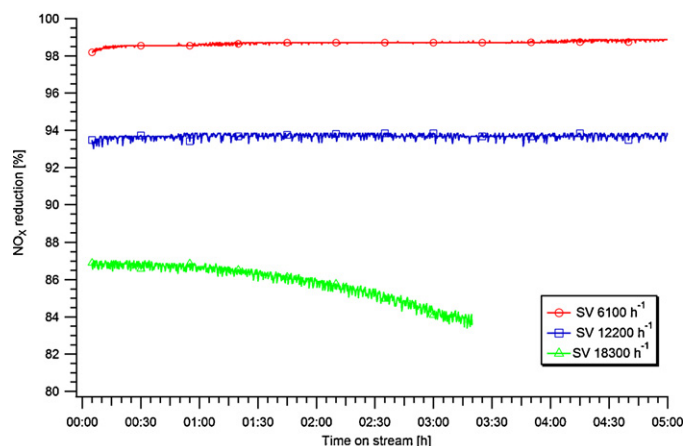


Fig. 5. NO_x reduction for 6100 (○), 12200 (□) and 18,300 h^{-1} (△). Feed gas composition: 500 ppm NO, 500 ppm NH_3 , 8% O_2 , 500 ppm SO_2 and 4% H_2O (300 °C).

Table 4Influence of H₂O and CO₂ on the NO_x reduction performance. Feed gas composition: 500 ppm NO, 500 ppm NH₃, 8% O₂, 0–6% H₂O (350 °C and 12,200 h⁻¹).

Step [0.5 h/step]	H ₂ O [%]	NO _x reduction [%]	NH ₃ conversion [%]	N ₂ O formation [ppm]
Step 1	0	86.0	87.5	8.5
Step 2	2	82.7	89.4	1.1
Step 3	0	86.7	88.4	8.9
Step 4	4	82.4	84.1	1.1
Step 5	0	87.1	88.2	9.1
Step 6	6	82.2	82.9	1.2
Step 7	0	87.4	88.3	9.2

stable at temperatures above 300 °C, while at 250 °C showing an instant decrease in catalytic activity (93%) followed by a continuous decrease (Fig. 4). Further, changing the space velocity results in a direct effect on the catalytic activity (Fig. 5). The two lower space velocities (6100 and 12,200 h⁻¹) allow stable activity, while the higher space velocity (18,300 h⁻¹) gives rise to a continuous decrease in catalytic activity. The final experiment, investigating the effect of sulfur concentrations at different temperatures, shows high and stable catalytic activities at 350 °C and 300 °C, while a significant drop in the catalytic activity is observed at 250 °C for both 250 ppm and 750 ppm SO₂ (Fig. 6). At 250 °C and 750 ppm SO₂ a continuous decrease in activity is observed.

3.4. Temperature programmed desorption

In order to evaluate the influence of SO₂ on the ammonia desorption, temperature programmed desorption (TPD) experiments were conducted (Table 2n). The results are illustrated in Fig. 7.

The TPD curves show a maximum in NH₃ desorption around 150 °C and a shoulder above 225 °C in both presence and absence of SO₂. This indicates two types of adsorption sites for NH₃ on the sample surface, one weaker and one stronger interaction with NH₃. At 150 °C the NH₃ desorption is higher without SO₂ in the feed, while the desorption peak around 275 °C is slightly higher in the presence of SO₂. In total the amount of adsorbed ammonia is slightly higher in the absence of SO₂ (about 3.5%).

4. Discussion

Considering the results for sample A it is evident that the NO_x reduction rate is dependent both on the space velocity and on the reaction temperature (Table 3). This is illustrated by comparing the NO_x reduction at SV 18,300 h⁻¹/300 °C and SV 12,200 h⁻¹/250 °C; of which both are in the range of 76%. Further, the steady state

NO_x reduction for sample B is in the range of 94–99% with a rather weak dependence on reaction temperature, which may be ascribed to the low space velocity (5700 h⁻¹) (Table 3). This is similar to the NO_x reduction activity for the sample A measurements at SV 6100 h⁻¹ (93–97%). A slight increase in NO_x reduction is noted for sample B in comparison to sample A (at SV = 6100 h⁻¹), which may be explained by the lower space velocity (5700 h⁻¹) for sample B. Hence, the comparable results for samples A and B at low space velocity, renders the use of a small sample (sample A) possible, which widens the reaction conditions that can be used. However, sample A only contains 12 cells, compared to 100 cells for sample B, implying that even a small variation in, e.g. the wash coat composition may influence the result for sample A to a larger extent than for sample B.

The catalytic activity for NO_x reduction with increasing SO₂ concentrations (100–1100 ppm) over sample A is increasing with increasing concentration of SO₂ in the reaction gas mixture together with increased N₂O formation (Fig. 2). These results are supported by earlier studies regarding the influence of SO₂ on lean NO_x reduction by ammonia over a V₂O₅/AC (activated carbon) catalyst at low temperatures (180–250 °C) [16–18]. According to Zhu et al. [17] it is suggested that the SO₂ is adsorbed and oxidized to SO₃ on the vanadium surface and then migrates to the carbon surface where it converts to sulfate species through reaction with H₂O. The formation of SO₃ is confirmed by the data in Fig. 2 and also suggested by Orsenigo et al. [19] as a first step to formation of sulfate species. The formed sulfate species act as new acid sites, which improves the NH₃ adsorption and thereby enhances the SCR activity. During the SCR reaction, in the presence of SO₂ at a temperature at around 180–250 °C, the formed sulfate species stay on the catalyst surface, while the ammonium ions react with NO continuously to avoid the formation and deposition of excess ammonium sulfate salts on the catalyst surface resulting in the catalyst being promoted but not poisoned by SO₂. Further, Zhu et al. [18] found that the promoting effect of SO₂ on a V₂O₅/AC (Sn-doped) is attributed to the

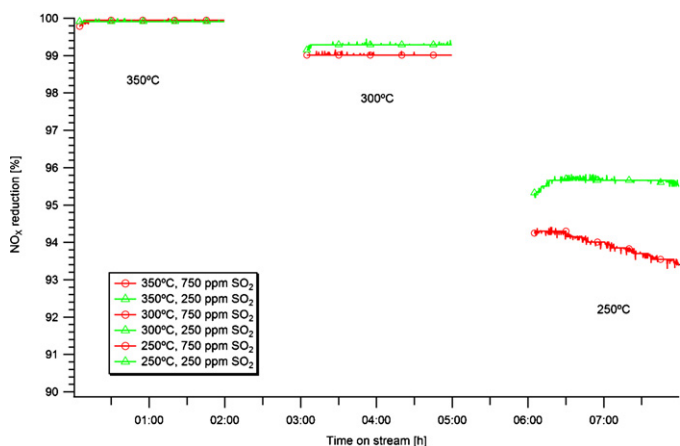


Fig. 6. NO_x reduction at 350, 300 and 250 °C for 250 (Δ) and 750 ppm SO₂ (○). Feed gas composition: 500 ppm NO, 500 ppm NH₃, 8% O₂, 250 and 750 ppm SO₂ and 4% H₂O (SV 6100 h⁻¹).

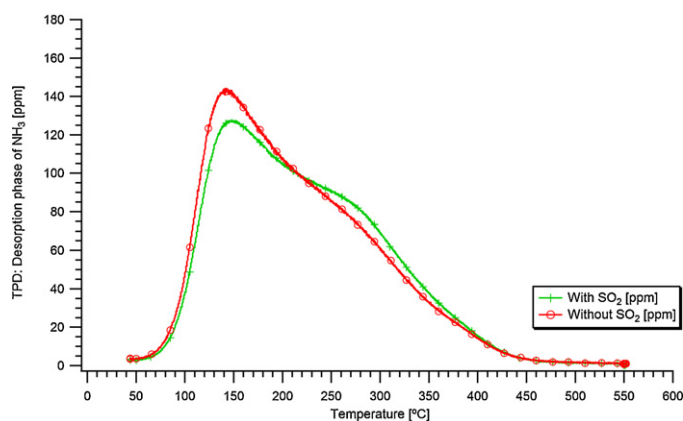


Fig. 7. Influence of SO₂ on the desorption of NH₃, using TPD. Feed gas composition: 500 ppm NH₃ during adsorption, desorption during temperature ramp with/without 500 ppm SO₂ (12,200 h⁻¹).

formation of sulfate species on the catalyst surface, which provides new Brønsted acid sites that increases the ammonium adsorption and the catalytic activity. However, the effect of the formed sulfate species is suggested to be two folded: (1) it provides acid sites for ammonium adsorption and thus enhancing the catalytic activity, (2) the sulfate species react with ammonia and transform into ammonium sulfate salts, such as NH_4HSO_4 and $(\text{NH}_4)_2\text{S}_2\text{O}_7$, which may plug the catalyst pores resulting in catalytic deactivation. It was also found by Huang et al. [16] that SO_2 promotes the SCR activity, over a $\text{V}_2\text{O}_5/\text{AC}$ catalyst, in the absence of H_2O , while in the presence of H_2O it speeds the deactivation. The two folded effect of SO_2 is attributed to the SO_4^{2-} formed on the catalyst surface which stays as ammonium sulfate salts on the surface. In the absence of H_2O a small amount of the salts are deposited on the catalyst surface resulting in a promoted SCR activity, while in the presence of H_2O the deposition rate of ammonium sulfate salts becomes much higher resulting in pore blocking and related catalytic deactivation.

The SCR reaction mechanism over a $\text{V}_2\text{O}_5/\text{TiO}_2$ catalyst typically involves two types of sites, where NH_3 adsorbs on a Brønsted acid site ($\text{V}-\text{OH}$), which in combination with a shift in oxidation state of a $\text{V}=\text{O}$ site catalyze the reduction of gas-phase NO [20]. Guo et al. [21] studied the effect of sulfate species on a $\text{V}_2\text{O}_5/\text{TiO}_2$ catalyst and proposed that SO_2 is oxidized to SO_3 over V_2O_x sites, which subsequently forms sulfate species on TiO_2 . They state that vanadium and hydroxyl ions are highly mobile under high-temperature reaction conditions (350–400 °C) in the presence of water, which leads to migration of SO_3 from a vanadium site to a neighboring $\text{Ti}-\text{OH}$ site forming a $\text{S}-\text{OH}$ group. This $\text{S}-\text{OH}$ group can also act as a Brønsted acid site, which increases the ammonia adsorption capacity at these conditions. Further, Kijlstra et al. [22] investigated the promotion and deactivation of a $\text{V}_2\text{O}_5/\text{TiO}_2$ SCR catalyst by SO_2 at low temperature, below 200 °C, and it was found that at lower V_2O_5 loadings, the surface of the catalysts can be sulfated by SO_2 , which gives rise to enhanced Brønsted acidity and to a higher SCR activity. On the other hand, at higher V_2O_5 loadings (6 wt.%) the SO_2 oxidation increases, followed by increased ammonium sulfate $(\text{NH}_4)_2\text{SO}_4$, formation and deposition, which overrules the promoting effect and leads to deactivation of the catalyst.

The observed promoting effect by SO_2 is thus suggested to be attributed to the formation of new Brønsted acid sites ($\text{S}-\text{OH}$) that enhance the NH_3 adsorption and thereby promote the NH_3 reaction with NO .

The influence of H_2O has been observed earlier [16,23] over $\text{V}_2\text{O}_5/\text{AC}$ catalysts and the results indicate an inhibiting effect on the NO reduction, which is suggested to be caused by competitive adsorption of H_2O and the reactants, such as NH_3 and/or NO on vanadia sites. It is also suggested that the effect of H_2O is independent of the vanadia loading. The influence of H_2O has also been investigated on other types of catalysts targeting selective catalytic reduction of NO , such as modified activated carbon fibres [24] and $\text{MnO}_x/\text{Al}_2\text{O}_3$ [25]. It was suggested that H_2O inhibits NO reduction at low temperatures (below 250 °C) due to competitive adsorption. However, even in the presence of water an excess of adsorbed ammonia was observed on the catalyst surface [25] and the decreased SCR reaction rate is considered to be caused by decreased adsorption of weakly bound nitric oxide.

Further, the inhibiting effect of H_2O on the N_2O formation, supported by, e.g. [25,26]. Kijlstra et al. [25], show a reversible and positive effect on the N_2 selectivity for $\text{Mn}/\text{Al}_2\text{O}_3$ at 325 °C and Mn_2O_3 at 150 °C, where the inhibition of ammonia oxidation and the non-selective catalytic reduction of nitric oxide are suggested to be stronger than the inhibition of the SCR reaction. According to Bagnasco et al. [26], who studied the selective reduction of NO with NH_3 over an iron-vanadyl phosphate catalyst, the addition of 1000 ppm H_2O (at 200–400 °C) results in a decrease in N_2O formation, thus enhancing the reaction selectivity. This behavior is

ascribed to an inhibiting effect of water on the NH_3 oxidation. Hence, despite the different types of SCR catalysts studied, these results support the observed inhibition effect by H_2O on the N_2O formation reported in this work.

The addition of H_2O , in absence of SO_2 , at a reaction temperature of 350 °C and SV of 12000 h^{-1} is observed to have a twofold effect on the SCR activity; inhibition of the NO_x reduction (from about 87% down to 82%) and inhibition of the N_2O formation (from about 9 ppm down to 1 ppm). The effect of H_2O seems to be fairly independent of the H_2O concentration (2–6%). The decreased NO_x reduction by H_2O is suggested to be attributed to competitive adsorption of H_2O on vanadia sites and the reactants such as NH_3 and/or NO , while the inhibition of the N_2O formation may be attributed to reduced activity for ammonia oxidation.

The prolonged effect of SO_2 exposure was investigated over sample A (Table 2h) and the NO_x reduction remained stable for 6 h after 1 h of SO_2 exposure (350 °C and SV 6100 h^{-1}). This eliminates any exothermic effects, causing the enhancement, that may have occurred due to SO_2 being oxidized to SO_3 . Further, this is consistent with a stable promoting effect of SO_2 and that NH_3SO_4 is unstable at this temperature.

Further, when continuously adding H_2O , separately, to the gas feed (Table 2j) over sample A, the lean NO_x reduction performance is stable at 97%. However, the effect of H_2O seems to be very dependent on the space velocity, e.g. comparing the results in Table 4 (SV 12,200 h^{-1}) with a NO_x reduction of approximately 82%. Thus, in the presence of H_2O the NO_x reduction seems even more sensitive to space velocity than in the absence of water. This is in agreement with competitive adsorption of H_2O and the reactants.

The results presented in Fig. 3 indicate a promoting effect of SO_2 on the NO_x reduction, higher for increasing SO_2 concentrations (Table 2f). The catalytic activity during heating is observed to increase with increased SO_2 concentration (at temperatures above 230 °C), while more pronounced during cooling.

At lower temperatures the catalytic activity is similar for all SO_2 concentrations. During the cooling process there is an obvious promotional effect from SO_2 , in the whole temperature range. This effect seems to be permanent since the higher activity seen in the presence of SO_2 is sustained also after removal of SO_2 from the feed gas. The presence of H_2O gives reduced activity during both heating and cooling. These observations are consistent with a scenario where the addition of SO_2 to the catalyst has two different effects; the formation of stable Brønsted acid sites that enhance the activity, and the formation of ammonium sulfate that inhibit the SCR activity. These salts seem to decompose at around 230 °C and explain the higher activity with SO_2 at higher temperature in the heating ramps. This decomposition is observed as a shoulder in the TPD curve presented in Fig. 7. Overall the TPD results suggest the formation of ammonium sulfate salts at lower temperatures and start of decomposition at an approximate reaction temperature of 230 °C. In the presence of SO_2 the stored ammonia likely reacts to form ammonium sulfate salts, which needs higher temperature to decompose and desorb than NH_3 . Though, the total desorbed NH_3 is higher in the absence of SO_2 .

During the cooling ramps the ammonium sulfate has not been formed and only the promoting effect of SO_2 is observed. Further, comparing the two experiments without SO_2 (at the end of each ramp series) one can conclude that there is a promoting effect remaining even without SO_2 present, while the ammonium sulfate has decomposed. Finally, the lower NO_x reduction in the presence of H_2O is in agreement with competitive adsorption of H_2O and the reactants.

Considering the influence of temperature on the NO_x reduction, in the presence of 500 ppm SO_2 and 4% H_2O , and at low space velocity (6100 h^{-1}) the results show a slight increase of the catalytic activity over time at 350 °C, constant reduction over time

at 300 °C and a continuous decrease with time at 250 °C (Fig. 4). These results can be compared with the steady state NO_x reduction without SO₂ and H₂O, Table 3, where the NO_x reduction is in the range of 97% at both 300 °C and 350 °C. This implies that the effects of SO₂ and H₂O are minor at low space velocities at temperatures above 300 °C. One possible explanation to the decrease in activity at 250 °C is the formation and deposition of ammonium sulfate salts, which is consistent with the previous discussion. This has also been reported for V₂O₅/AC catalysts exposed to SO₂ and H₂O [12,16]. According to Huang et al. [12] a higher content of H₂O (2.5–20%) results in a higher deactivation rate of the catalyst. The addition of H₂O increases the formation rate of ammonium sulfate salts and decreases the reaction rate between the ammonium sulfate salts and NO, while the SO₂ does not affect the reaction rate. Further, according to Huang et al. [16] a higher V₂O₅ loading increases the oxidation activity of the catalyst and gives a higher formation rate of the ammonium sulfate salts. It was also found that a higher space velocity results in higher formation rate of ammonium sulfate salts, whereby it is suggested that the catalytic deactivation can be reduced or eliminated by reduced V₂O₅-loading and/or reduced space velocity.

Overall, the present results suggest that at a space velocity of 6100 h⁻¹ and temperatures above 300 °C the NO_x reduction remain stable, even in the presence of combined SO₂ and H₂O, and is also comparable to steady state conditions in the absence of both SO₂ and H₂O. However, at 250 °C it is suggested that an increased deposition of ammonium sulfate salts gives rise to a decrease of the NO_x reduction, possibly by pore plugging.

The long term experiments show that there is a continuous deactivation at low temperatures (Fig. 4), high space velocities (Fig. 5) and at high SO₂ concentrations (Fig. 6). This is all consistent with the formation of ammonium sulfates that inhibits the SCR reaction.

5. Conclusions

This paper reports on the effects of SO₂ and H₂O concentrations, reaction temperature and space velocity on the SCR activity for a commercial vanadia-based washcoated urea-SCR catalyst for marine applications.

In general, addition of SO₂, in absence of water, promotes the NO_x reduction and the NH₃ conversion along with an increased formation of N₂O. These effects seem to be more pronounced with increasing SO₂ concentration and relatively independent of temperature. The promoting effect on the NO_x reduction is sustained also after removing SO₂ from the feed gas. On the contrary, the addition of H₂O, in absence of SO₂, results in a decreased NO_x reduction and an inhibition of the N₂O formation. These effects are reversible and fairly independent of both water content and temperature.

In the presence of both SO₂ and water the activity for NO_x reduction decreases, in particular at high concentrations of SO₂, low temperatures and high space velocities. This can possibly be explained by the formation of ammonium sulfate salts at low temperatures, which is also consistent with the results from the TPD experiments where, in the presence of SO₂, a higher desorption of ammonia is noted at the decomposition temperature of ammonium sulfate salts. In conclusion, these problems can thus be avoided by keeping the temperature high enough (i.e. above 300 °C) and the

space velocity and the SO₂ concentration low enough (i.e. below 12,200 h⁻¹ and 500 ppm, respectively).

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